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Technical Report No. 2

Model Filled Polymers II. Stability of Polystyrene Beads in a
Polystyrene Matrix

by

K. Gandhi, M. Park, L. Sun, D. Zou, C. X. Li*
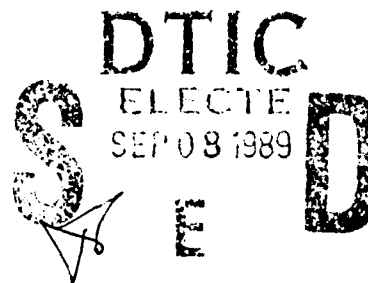Y. D. Lee*, J. J. Aklonis*, and R. Salovey

Prepared for Publication

in the

University of Southern California
Department of Chemical Engineering
*Department of Chemistry
Los Angeles, California 90089-1211

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SEP 08 1989
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September 1, 1989

89 9 8 110

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

Technical Report No. 2

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
The University of Southern California	MC 1211	Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Department of Chemical Engineering, MC 1211 University of Southern California Los Angeles, CA 90089-1211	800 North Quincy Street Arlington, VA 22217-5000

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
ONR/DARPA		ONR N00014-88-K-0302

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
800 North Quincy Street Arlington, VA 22217-5000				

11. TITLE (Include Security Classification)

Model Filled Polymers II. Stability of Polystyrene Beads in a Polystyrene Matrix

12. PERSONAL AUTHOR(S)
K. Gandhi, M. Park, L. Sun, D. Zou, C. X. Li, Y. D. Lee, J. J. Aklonis, and R. Salovey

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 5/1/88 TO 8/30/89	September 1, 1989	18

16. SUPPLEMENTARY NOTATION

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB GROUP	Polymer Composites; Filled Polymers; Monodisperse Polystyrene Beads; Thermomechanical Degradation; Thermal Stability

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Thermomechanical degradation, as a result of mixing at 175°C during the preparation of polystyrene composites containing monodisperse (0.45μm) crosslinked polystyrene beads, often leads to a uniform decrease in rheological properties on increasing the concentration or on reducing the crosslink density of the beads. The extent of such degradation depends on the molecular weight of polystyrene and on the crosslink density of the polystyrene beads. Scission fragments from decomposed beads may induce free radical degradation of the polystyrene matrix. Degradation during mixing of the beads and the matrix is suppressed by mixing crosslinked beads in a polystyrene solution, and removing the solvent, or by melt mixing after adding 0.2% BHT. Polystyrene beads and composites show thermally induced weight loss on heating above 330°C in nitrogen or above 250°C in air. Networks of increased crosslink density are of enhanced thermal stability on heating in the absence of shear.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr. JoAnn Milliken	(703) 696-4409	ONR

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted

Model Filled Polymers

II. Stability of Polystyrene Beads in a

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ABSTRACT

Thermomechanical degradation, as a result of mixing at 175°C during the preparation of polystyrene composites containing monodisperse (0.45μm) crosslinked polystyrene beads, often leads to a uniform decrease in rheological properties on increasing the concentration or on reducing the crosslink density of the beads. The extent of such degradation depends on the molecular weight of polystyrene and on the crosslink density of the polystyrene beads. Scission fragments from decomposed beads may induce free radical degradation of the polystyrene matrix. Degradation during mixing of the beads and the matrix is suppressed by mixing crosslinked beads in a polystyrene solution, and removing the solvent, or by melt mixing after adding 0.2% BHT. Polystyrene beads and composites show thermally induced weight loss on heating above 330°C in nitrogen or above 250°C in air. Networks of increased crosslink density are of enhanced thermal stability on heating in the absence of shear.

Model Filled Polymers

II. Stability of Polystyrene Beads in a

Polystyrene Matrix

INTRODUCTION

Unusual rheological effects often result from the inclusion of fillers in ordinary thermoplastics [1-3]. Filled systems can be highly non-Newtonian. High concentrations of surface active fillers may agglomerate and preclude flow, exhibiting a yield phenomenon in steady shear flow and frequency independent moduli in oscillatory shear flow [4-8]. The viscosity of polymers containing small concentrations of inert filler may approach or even fall below the viscosity of the pure polymer in steady shear at high shear rates [5,6] or have dynamic moduli close to those of the pure polymer at high frequency [7,8]. In order to elucidate such unique flow behavior, it is necessary to design model systems containing well characterized fillers and matrices. Moreover, it is essential to avoid permanent thermal or mechanical degradation on mixing or testing filler and matrix. We are pursuing an extensive program aimed at clarifying the basic rheology of polymer matrices containing monodisperse polymeric beads. In studies on systems of polystyrene beads incorporated into polystyrene, we encountered some surprising rheological changes. In this paper we investigate and attempt to elucidate this behavior.

EXPERIMENTAL DETAILS

MATERIALS

Polystyrene (pellets) is obtained from Dow Chemical Co. (Dow Styron 685) and has a weight average molecular weight of 250,000 g/mol and a polydispersity of 2.9 from gel permeation chromatography of tetrahydrofuran solutions.

Monodisperse crosslinked polystyrene beads are prepared using several stirring techniques in a persulfate initiated emulsifier-free emulsion polymerization [9]. As described [9], bead sizes are measured by scanning electron microscopy and different crosslink densities obtained by varying the ratio of divinylbenzene/styrene. The bead size used for these studies approximated 0.45μm.

2,6-di-tert-butyl-4-methylphenol (BHT) is 99% purity product from Aldrich Chemical Co.; methanol and tetrahydrofuran (HPLC grade) are from Fisher Scientific Co.

MIXING

Several techniques are used for mixing polystyrene beads and polystyrene matrix. Polystyrene matrix is first melted in an internal mixer (Brabender Plasticoder) at 175° C and dry beads are added to the mixer. The mixture is agitated at 50 rpm for 7.5 minutes followed by 100 rpm for another 7.5 minutes at 175°C. Polystyrene beads and pellets could also be dry-blended and then mixed in the internal mixer at 175°C. Crosslinked polystyrene beads are also dispersed in a solution of polystyrene in tetrahydrofuran, and the polymers precipitated by the addition of excess methanol. The mixture of beads and matrix were isolated and dried to constant weight. Alternatively, latexes of crosslinked and uncrosslinked polystyrene beads are mixed and co-coagulated by freezing or centrifuging, isolated and dried to constant weight. After mixing, samples are compression molded in a hydraulic press (Preco) at 175°C and 1.5×10^7 Pa for 15 minutes, while attempting to remove trapped air bubbles.

RHEOLOGICAL STUDIES

A rheogoniometer (Weissenberg, Model R19) with cone and plate geometry is used for steady and oscillatory shear measurements. The cone angle is 0.034 radians and the plate radius is 2.5 cm. Samples were 2.5 cm radius disks, 1 mm thick. Rheological data were taken at 200°C. The viscosity, η, and first normal stress difference, N_1, are measured at various shear rates, $\dot{\gamma}$, in steady shear flow. Storage modulus, G', loss modulus, G'', and

dynamic viscosity, η', are measured at different frequencies, ω, in small amplitude oscillatory shear flow. The strain amplitude is 5%. Because of the destructive nature of steady shear measurements at high shear rates, the dynamic experiment is run first and the reversibility of dynamic and steady shear testing (the latter, at low shear rates) assessed by repeated runs.

CHARACTERIZATION

Bead size and bead dispersion in the polystyrene matrix are examined by scanning electron microscopy (Stereoscan 360, Cambridge Instruments Ltd.) using LaB6 filament and a voltage of 10 KV. Samples were sputter coated with gold and palladium prior to microscopy.

The molecular weight of the polystyrene matrix and uncrosslinked beads are determined by gel permeation chromatography (GPC). GPC is conducted with a Waters (M-6000A) instrument, equipped with five microstyragel columns, or with a high performance liquid chromatograph (Perkin-Elmer Tri-Det HPLC), equipped with a 5μm mixed bed organic size exclusion column (PE/PL GEL). Both instruments are calibrated with polystyrene standards and toluene was injected to correct for fluctuations in flow rate and chart speed. The tetrahydrofuran mobile phase flow rate is 1.0 ml/min. and ultraviolet detectors are used.

The glass transition temperature is determined by differential scanning calorimetry (Perkin-Elmer DSC-4) for polystyrene beads and for bead filled polystyrene [9,10].

The thermal stability of polystyrene beads and bead filled polystyrene is measured by thermogravimetric analysis (Perkin-Elmer TGS-2) at a heating rate of 20°C/min in nitrogen and air atmospheres.

RESULTS

The variation of steady shear viscosity and first normal stress difference as a function of shear rate, and the dynamic moduli as a function of frequency, are measured for

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polystyrene containing monodisperse 0.45μm crosslinked polystyrene beads varying in crosslink density at several filler loadings at 200°C. Mixing for these studies was accomplished at 175°C in an internal mixer. The steady shear viscosity, first normal stress difference and dynamic moduli for filled systems are all lower than the matrix. For 5% loading, rheological properties decreased uniformly with decreasing crosslink density. Steady shear data are illustrated in Figure 1. However, for 10% loading, the maximum reduction in these properties occurred at 2% crosslink density, as shown in Figure 2 for steady shear rheology. In general, increased filler loading leads to increased reductions in rheological properties (Figure 3).

The effect of mixing on the molecular weight of the polystyrene matrix and uncrosslinked beads was studied by gel permeation chromatography (GPC) in tetrahydrofuran solution. Pure polystyrene pellets repeatedly exhibited a weight average molecular weight ($\overline{M}_w$) of 250,000±10,000. Following mixing in the internal mixer (Brabender) for 15 minutes at 175°C, the GPC curve was virtually unchanged. Similarly, the zero shear viscosity of the pure polystyrene is the same (1.4 x 10^4 Pa · sec), before and after 15 minutes mixing. If the polystyrene were mixed for 25 minutes at 175°C, the chromatogram was slightly displaced and $\overline{M}_w$ reduced to 220,000. Similarly, steady shear viscosities are reduced (to 1.1 x 10^4 Pa · sec) by such treatment. The molecular weights of polystyrene beads synthesized by us in emulsifier free emulsion polymerization [9] are generally much higher. A large batch of uncrosslinked polystyrene beads gave $\overline{M}_w$ equal to 540,000 (repeatedly). If 10 weight percent of these beads are mixed with the pure polystyrene (matrix) for 15 minutes at 175°C in the internal mixer, the GPC curve was displaced to lower molecular weights, especially for high molar masses, giving $\overline{M}_w$ of 120,000. If the polystyrene beads and matrix were solution mixed (in tetrahydrofuran), $\overline{M}_w$ equaled 260,000. Similarly, if 0.2 or 0.5 weight percent BHT were added prior to melt mixing

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(Brabender) for 15 minutes at 175°C, $\bar{M}_w$ equaled 260,000. With 5% loading of these beads in polystyrene containing 0.2% BHT, $\bar{M}_w$ equaled 250,000. At 20% loading, the corresponding value of $\bar{M}_w$ was 300,000.

Rheological behavior in steady shear of 10% bead filled systems after mixing in solution or in the presence of BHT is illustrated in Figure 4. Analogous results are observed in oscillatory shear.

The thermal stability of monodisperse polystyrene beads (0.45µm) of various crosslink densities, the polystyrene matrix polymer and composites of beads dispersed in the matrix, is assessed by thermogravimetric analyses in nitrogen and air atmospheres. In nitrogen, the onset of weight loss is detected at ~330°C for uncrosslinked beads. Here, uncrosslinked beads, whether initiated by potassium persulfate or hydrogen peroxide, are more stable than the polystyrene matrix polymer, showing an increase of 6°C for 50% weight loss. With increase in crosslink density of the beads, by copolymerizing with 1 and 5% divinylbenzene, the thermal stability is further enhanced by 4 and 6°C, respectively.

In an air atmosphere, the onset of weight loss was detected at ~250°C for uncrosslinked polystyrene beads, which were 5°C less stable than the polystyrene matrix, for 50% weight loss. Again, the thermal stability of the beads increased with crosslink density. Here, the matrix polystyrene was of similar thermal stability to polystyrene beads crosslinked with 1% divinylbenzene. For polystyrene beads crosslinked with 5% divinylbenzene, the thermal stability in air increased by 17°C. Polystyrene beads initiated with hydrogen peroxide are more stable to thermal decomposition in air, than beads initiated with potassium persulfate.

Polystyrene composites, containing 10% beads of various divinylbenzene contents, show similar thermal stability in nitrogen atmosphere. However, composites containing beads crosslinked with 5% divinylbenzene have the highest thermal stability, compared to composites filled with beads of lower crosslink densities. The addition of BHT antioxidant

increases the thermal stability of such composites, raising the onset of thermal decomposition by ~10°C.

DISCUSSION

Ordinarily, the inclusion of filler particles increases rheological properties, such as steady shear viscosity and dynamic moduli, of linear polymers [1, 11, 12]. The observation that such properties are decreased by the addition of monodisperse polystyrene beads is surprising. That such properties decrease uniformly with increasing crosslink density of the polystyrene beads, as shown in Figure 1, is still more surprising. A careful study of the molecular weight of the polystyrene matrix, by GPC, explains this phenomenon. As a result of mixing a polystyrene composite, actually, a blend, consisting of uncrosslinked polystyrene beads in a polystyrene matrix, for 15 minutes in an internal mixer at 175°C, the overall molecular weight is reduced. For example, at a 10% loading, the molecular weight ($\bar{M}_w$) of the composite was calculated to be 280,000. However, the weight average molecular weight, observed after 15 minute mixing at 175°C, was 120,000. The high molecular weight polystyrene beads, of $\bar{M}_w$ = 540,000, are "readily" thermomechanically degraded. Such degradation may involve a free radical mechanism, with the formation of alkyl and scission fragment free radicals. The formation of radicals, preferentially in the high molecular weight beads [13-15] , initiates free radical breakdown of the matrix.

When the beads are crosslinked, dangling polystyrene chains, or cilia, are primarily subjected to chain scission. With increasing crosslink density of the beads, the number of cilia is decreased, leading to enhanced stability. Free radicals generated by fragmentation of cilia can initiate scission reactions in the polystyrene matrix. As a result, the stability of the composite appears to increase with crosslink density (Figure 1). Since we are dealing with a random scission process, the dependence of rheological properties on crosslink density is not

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always clear (Figure 2). However, increasing the concentration of bead filler, often causes further reductions in molecular weight stability (Figure 3).

There are several reasons why uncrosslinked polystyrene beads are less stable to mixing at elevated temperatures than the polystyrene matrix. From gel permeation chromatography, the beads have $\bar{M}_w = 540,000$, while the matrix has $\bar{M}_w = 250,000$. It is well known that thermomechanical stability depends inversely on molecular weight and is reduced for very high molecular weight polymers [15, 16]. Further, the beads studied were prepared by persulfate initiated polymerization, which leads to sulfate (among other) end groups [17-21]. We have seen that hydroxy terminated polystyrene from peroxide initiation is more stable than sulfate terminated polystyrene, in thermogravimetric analysis [9]. Following mixing at 175°C, the polystyrene, used for the matrix, is, itself, of marginal stability. Even the matrix polystyrene, of initial $\bar{M}_w = 250,000$, is slightly degraded in molecular weight on mixing for 25 minutes at 175°C.

In order to avoid the thermomechanical degradation of polystyrene filled with uncrosslinked polystyrene beads, BHT antioxidant was added [22]. At 5, 10 and 20% loading of beads, the resulting molecular weights were very close to calculated values. 0.2 weight % antioxidant (BHT) was found to be adequate to prevent degradation in our systems. Another way to avoid degradation, was to mix uncrosslinked polystyrene beads and matrix in tetrahydrofuran solution at 25°C. Following this process, for 10% beads, $\bar{M}_w$ is 260,000, identical to that of the composite mixed at 175°C in the presence of BHT.

If we proceed to use crosslinked polystyrene beads as filler, we can no longer easily measure stability by GPC. However, if the beads were carefully removed by repeated filtration, evidence of matrix degradation was observed in GPC. Such degradation could be prevented by adding 0.2% BHT. Ordinarily, the stability of polystyrene composites containing crosslinked polystyrene beads, is followed by rheogoniometry. Both in steady (Figure 4) and in oscillatory shear, 0.2% BHT appears to be adequate to prevent thermal degradation on mixing the composite for 15 minutes at 175°C. The rheological properties of

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samples mixed in solution at 25°C are very similar to the results of antioxidant protected mixing. Often, solution mixed samples are slightly plasticized by the presence of trapped tetrahydrofuran solvent (Figure 4). In the absence of BHT, beads induce further molecular weight degradation on mixing at 175°C (Figure 4). Cilia dangling from crosslinked polystyrene beads are particularly susceptible to chain scission during high shear mixing at elevated temperatures.

Thermal stability, in the absence of high shear mixing, may be inferred from weight loss measurements on heating samples during thermogravimetric analysis. Ordinarily, we compared temperatures corresponding to 50% weight loss. The temperature at the onset of weight loss was also reported, as indicated. In nitrogen atmosphere, thermal degradation is probably a random scission process, and thermal stability depends primarily on the number of covalent bonds. Thus, uncrosslinked beads, which are more than twice the molecular weight of the polystyrene matrix, are more thermally stable than the matrix. Increasing the number of covalent bonds by crosslinking, leads to further increases in decomposition temperatures. In air, thermal degradation may become increasingly sensitive to imperfections in the polymer chains and to oxidation induced by specific end groups. Now, the onset of weight loss is reduced by 80°C, compared to decomposition in nitrogen. Moreover, the uncrosslinked beads were less stable than the polystyrene matrix. However, again, the thermal stability of the beads increased with crosslink density. Since crosslinks are very effective in reducing the number of volatile fragments resulting from scission, even at specific sites, thermal stability increased markedly for beads crosslinked with 5% divinylbenzene. In general, network formation by crosslinking the polystyrene beads, enhances their thermal stability. Again [9], the end group on the polystyrene chain affects thermal stability.

Thermogravimetric analysis of polystyrene composites, filled with crosslinked polystyrene beads of various divinylbenzene contents, shows that thermal stability is not very sensitive to the crosslink density of a small concentration of component beads, in the absence of shear. However, enhanced thermal stability was detected for the system

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containing beads of highest crosslink density. Polystyrene composites increased in thermal stability by the addition of 0.2% BHT, as indicated by a 10°C increase in the temperature at the onset of weight loss.

CONCLUSIONS

The rheological properties at 200°C, of polystyrene containing monodisperse 0.45μm crosslinked polystyrene beads, appear to decrease uniformly on increasing the concentration of beads or on reducing the crosslink density of the beads. The steady shear viscosity, first normal stress difference and dynamic moduli for filled systems are all lower than for the polystyrene matrix alone. From gel permeation chromatography (GPC) studies, we conclude that thermal degradation of the polystyrene composite, as a result of intensive mixing in an internal mixer at 175°C, explains these observations. The extent of thermomechanical degradation depends on the molecular weight of polystyrene and on the crosslink density of the polystyrene beads. We suggest that high molecular weight polystyrene comprising the beads ($\bar{M}_w$ = 540,000) is more susceptible to chain scission on mixing, than the lower molecular weight matrix polystyrene ($\bar{M}_w$ = 250,000). Moreover, polystyrene molecules dangling from the surface of crosslinked beads (cilia), would be particularly subject to thermomechanical degradation. Resultant scission fragments from decomposed beads induce free radical degradation of the polystyrene matrix. Since the number of cilia decreases with increasing crosslink density of the beads, the stability of bead filled systems (to thermomechanical degradation) appears to increase with the degree of crosslinking of the beads. Degradation during mixing of the beads and matrix may be avoided by dispersing the beads in a polystyrene solution at 25°C, although, subsequent removal of solvent may be difficult. Similarly, inclusion of 0.2% free radical scavenger, BHT, suppresses thermomechanical degradation during mixing, for 15 minutes at 175°C.

The thermal decomposition and volatilization, of scission fragments in polymeric beads and bead filled systems, are readily accomplished by heating above 330°C in nitrogen or 250°C in air, during thermogravimetric analysis. The thermal stability of the polystyrene beads exceeds that of the polystyrene matrix in nitrogen atmosphere, probably because the molecular weight of the beads exceeds that of the matrix. In air or in nitrogen, the thermal stability of the beads increases with crosslink density, as we increase the number of covalent bonds. Networks of increased crosslink density are of increased thermal stability on heating in the absence of shear. Uncrosslinked polystyrene beads with hydroxyl end groups, from peroxide initiation, are more stable than uncrosslinked polystyrene beads with sulfate end groups, from persulfate initiation, to thermal decomposition in air. Compared to nitrogen atmosphere, chain scission is enhanced in air and may be more affected by specific chain imperfections and oxidation induced by end groups. In air or nitrogen, the presence of 0.2 weight percent BHT increases thermal stability.

ACKNOWLEDGEMENT

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LIST OF FIGURES

1. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with 5% polystyrene beads.

    O   pure polystyrene

    X   filled polystyrene, beads prepared with 1% divinylbenzene

    Δ filled polystyrene, beads prepared with 2% divinylbenzene

    ●   filled polystyrene, beads prepared with 5% divinylbenzene

2. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with 10% polystyrene beads of varied crosslink density.

    O   pure polystyrene

    X   filled polystyrene, beads prepared with 1% divinylbenzene

    Δ filled polystyrene, beads prepared with 2% divinylbenzene

    ●   filled polystyrene, beads prepared with 10% divinylbenzene

3. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with crosslinked polystyrene beads, prepared with 2% divinylbenzene at several loadings.

    O   pure polystyrene

    X   filled polystyrene containing 5% beads

    Δ filled polystyrene containing 10% beads

4. Steady shear viscosity (η) at 200°C and at several shear rates ($\dot{\gamma}$) of polystyrene filled with 10% by weight of uncrosslinked polystyrene beads.

    +   pure polystyrene

    O   filled polystyrene prepared by solution mixing

    Δ filled polystyrene prepared by melt mixing

    X   filled polystyrene prepared by melt mixing, containing 0.2% BHT

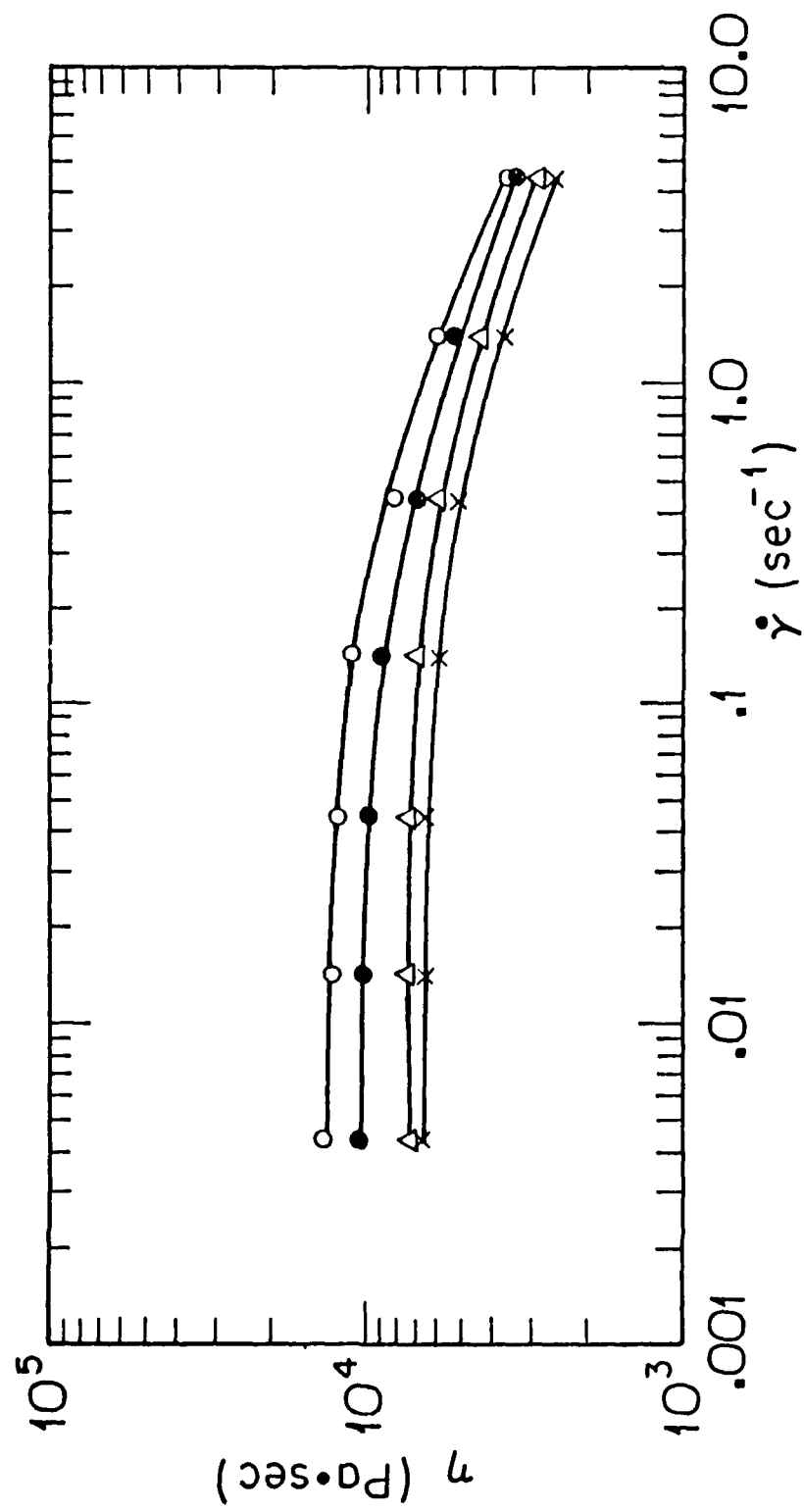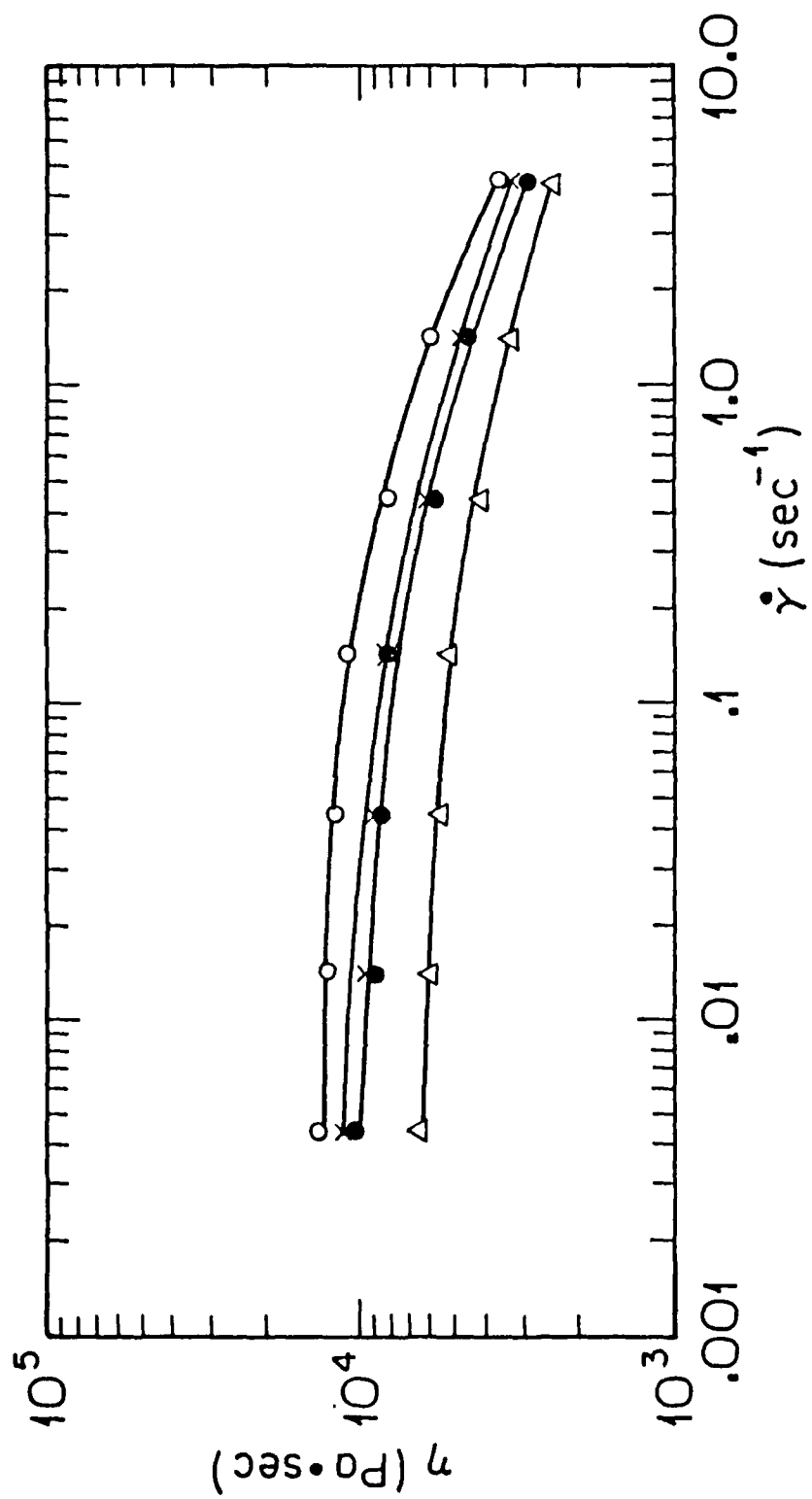   ●   filled polystyrene prepared by melt mixing, containing 0.5% BHT
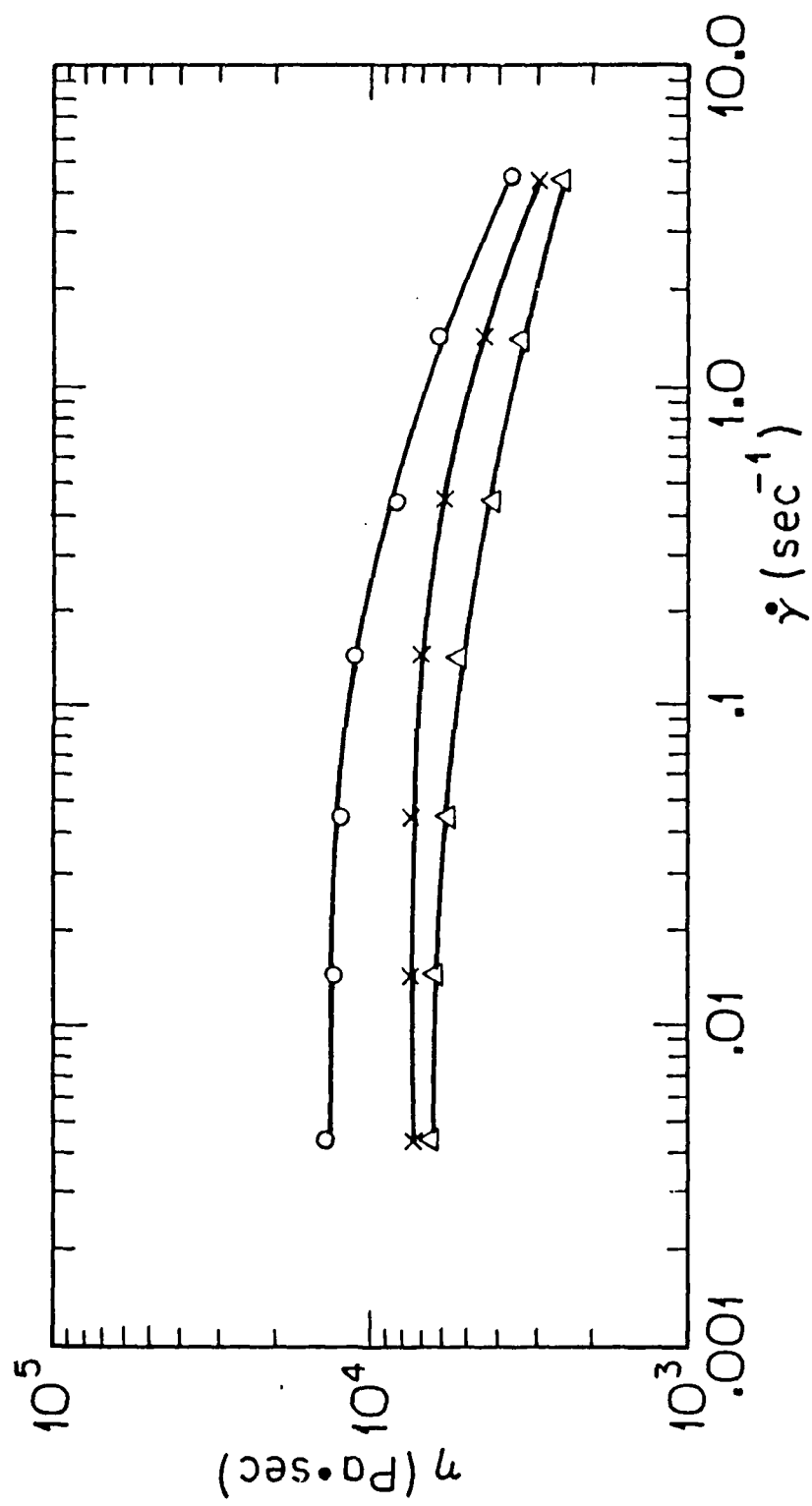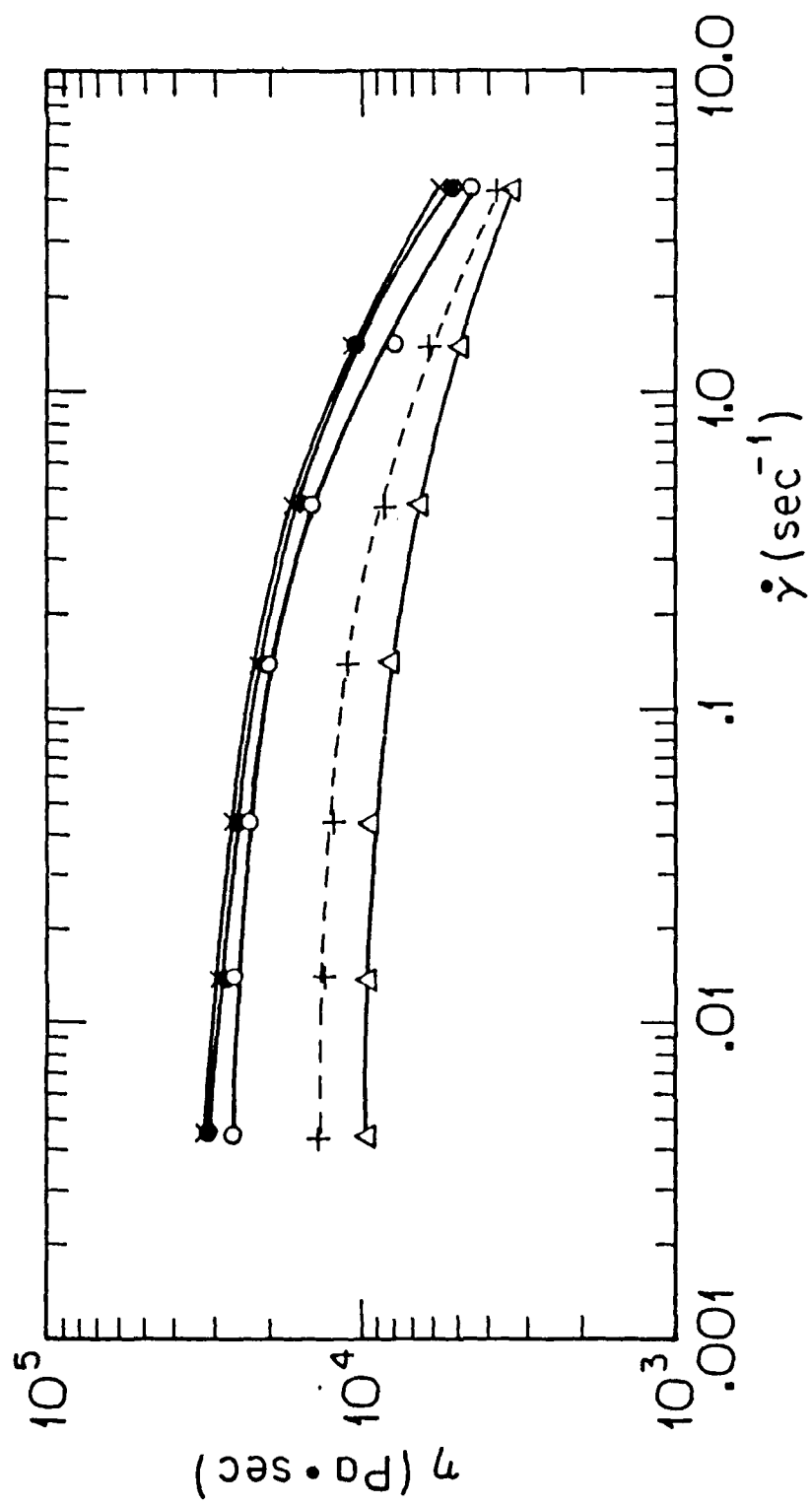
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FIGURE 1

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FIGURE 4

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